

Highlights from Recent Literature

1 Analytical

1.1 Flame Atomic Absorption Spectrometric Determination of Gold, Palladium and Platinum in Catalytic Converters

A simple procedure for the flame atomic absorption spectrometric detection of Au, Pd and Pt contents of the catalytic converters of the automobiles is proposed. M. Soylak, E. Buyuksekerici and L. Elci, Latif from the Department of Chemistry, Faculty of Art and Science, Erciyes University, Turkey, *Asian Journal of Chemistry* 2004, **16(3-4)**, 1625. The procedure includes the combination of solid phase extraction of Au, Pd, Pt on amberlite XAD-7 adsorption resin and flame atomic absorption spectrometric detection. The procedure was also applied to the detection of analytical contents of natural waters with satisfactory results.

2 Catalysis

2.1 Supported Gold Catalysts for Oxidation of Carbon Monoxide

A patent by H. Lansink-Rotgerink, J. Gerhardus I. Pietsch, M. Pohl, G. Klinger, B. Luecke, and H. Kosslick, from Degussa, Germany, Patent No. DE 10321273, A1 9.12.2004 describes a supported gold catalysts, consisting of a mixture of activated charcoal carrier with a disperse gold-support catalyst. The materials are manufactured by grinding the activated charcoal carrier with the gold catalyst by means of a mill. They are used for the oxidation of carbon monoxide at moderate temperatures.

2.2 Transient Studies on Carbon Monoxide Oxidation over Supported Gold Catalysts: Support Effects

The origin of support effects on the activity of supported gold catalysts was examined in details via the Temporal Analysis of Products (TAP) approach. M. Olea, Y. Iwasawa, from the Department of Chemistry, Graduate School of Science, The University of Tokyo, Japan, *Applied Catalysis, A: General* 2004, **275(1-2)**, 35. Supported catalysts derived from interaction of an Au-phosphine complex $\text{Au}(\text{PPh}_3)(\text{NO}_3)$ with as-precipitated titanium hydroxide $\text{Ti}(\text{OH})_4^*$ afforded remarkably high catalytic activity for low-temperature carbon monoxide oxidation compared to catalysts obtained by supporting $\text{Au}(\text{PPh}_3)(\text{NO}_3)$ to conventional titanium oxide TiO_2 . At 300 K, for a carbon monoxide to oxygen 1:1 ratio, carbon monoxide conversion was 50% on $\text{Au}/\text{Ti}(\text{OH})_4^*$ catalyst, but 1% only on Au/TiO_2 .

Single-pulse TAP experiments evidenced that, among the other factors, morphology and specific surface area of

catalyst supports have an influence on intraparticle diffusion and adsorption features, which in turn have an influence on the reaction rate. While for the mesoporous $\text{Au}/\text{Ti}(\text{OH})_4^*$ catalyst, its internal surface area is efficiently utilized equally to the external surface for carbon monoxide oxidation, for the micro-porous Au/TiO_2 catalyst, carbon monoxide oxidation reaction occurs pre-eminently on the external surface, because the internal diffusion was extremely slow. Based on pulse-response results, a new method to detect the intraparticle Knudsen diffusivity, D_p , was proposed. For argon on Au/TiO_2 , 1.4 times. $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ D_p calculated value was in good agreement with values reported in literature.

2.3 Carbon Monoxide Oxidation on Supported Platinum and Gold Catalysts in the Presence of Hydrogen

The low-temperature selective oxidation of CO on supported Pt- and Au catalysts in exhaust gas treatment was studied in the excess of H_2 and in the presence and absence of water. V. Tret'yakov, T. Burdeninaya and L. Berezina from the Inst. Neftekhim. Sint. im. A. V. Topchieva, RAN, Moscow, Russia, *Neftekhimiya* 2004, **44(3)**, 191. The results indicated that such catalytic systems ensure a high degree of CO conversion and a high selectivity within a temperature range of 50-150.degree. It was also found that under certain conditions, the reaction proceeds in a self-oscillating regime.

2.4 Synthesis of Ordered Mixed Titania and Silica Mesostructured Monoliths for Gold Catalysts

Mesostructured silica-titania mixed oxide monoliths, in which the nanocrystal titania is well dispersed inside the silicate framework, have been synthesized by a liquid crystal templating approach in combination with sol-gel processing. H. Zhu, Z. Pan, B. Chen, B. Lee, S. Mahurin, S. Overbury and S. Dai from the Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, USA, *Journal of Physical Chemistry B* 2004, **108(52)**, 20038. Control over the different hydrolysis and condensation rates of silicon and titanium alkoxides was achieved by complexation of the titanium species to the poly(ethylene oxide) (PEO) part of a block copolymer, such as Pluronic F108. The block copolymer serves two distinct functions: (a) as a structure-directing agent and (b) as a moderator of the hydrolysis rate of titanium alkoxide. The amorphous titania inside the silica framework is converted by calcination treatment into anatase phase TiO_2 incorporated on the silica. The structure and composition of the resulting material was characterized by X-ray diffraction, UV-visible absorption spectroscopy, Raman spectroscopy, and transmission electron microscopy. The monoliths have an ordered mesostructure with very small crystallites of anatase TiO_2 located within the mesopores. The authors show that the mixed oxide monoliths are excellent support materials for gold catalysts.

2.5 Influence of Gold on the Reduction Behaviour of Au-V₂O₅/CeO₂ Catalytic Systems: TPR and Kinetic Parameters of Reduction

The reduction behaviour of nine gold-vanadia/ceria and vanadia/ceria catalyst samples prepared by different methods has been studied using temperature programmed reduction. G. Munteanu, L. Ilieva, R. Nedyalkova and D. Andreeva from the Institute of Physical Chemistry, Romanian Academy, Bucharest, Romania, *Applied Catalysis, A: General* 2004, **277(1-2)**, 31. Fitting each computed TPR pattern to the experimental one, the kinetic parameters and the hydrogen consumption corresponding to all individual reduction processes were detected. It was shown that the gold content of every sample is reflected both by the values of parameters of the Sestak-Berggren function and by the dependence of the activation energy of reduction on the degree of reduction. The reduction behaviour of every sample has been studied taking into account the composition of each sample as well as the values of the kinetic parameters together with those of the Sestak-Berggren exponents and the dependence of the activation energy on the degree of reduction. It is shown that upon comparing the TPR results it is possible to select the most active catalytic systems in the complete oxidation of hydrocarbons.

2.6 The Structure of Catalytically Active Gold on Titania

The high catalytic activity of gold clusters on oxides has been attributed to structural effects (including particle thickness and shape and metal oxidation state), as well as to support effects. The authors, M. Chen and D. Goodman from the Department Chemistry, Texas A&M University, USA, *Science* (Washington, DC, United States) 2004, **306(5694)**, 252, have created well-ordered gold monolayers and bilayers that completely wet (cover) the oxide support, thus eliminating particle shape and direct support effects. High-resolution electron energy loss spectroscopy and carbon monoxide adsorption confirm that the gold atoms are bonded to titanium atoms. Kinetic measurements for the catalytic oxidation of carbon monoxide show that the gold bilayer structure is significantly more active (by more than an order of magnitude) than the monolayer.

2.7 Air Purification System Comprising Gold/Titanium Dioxide Photocatalyst

The invention by D. Wei, T. Vanderspurt, T. Obee, S. Hay, W. Schmidt, from the Carrier Corporation, USA, Patent No. WO 2004112958, A1, 29.12 2004 describes a gold/titanium dioxide photocatalytic/thermocatalytic coating simultaneously oxidizing volatile organic compounds and carbon monoxide that adsorb onto the coating into water, carbon dioxide, and other substances. The gold has a size less than 3 nm. When photons of the UV light are absorbed by the gold/titanium dioxide coating, reactive hydroxyl radicals are formed. When a contaminant is adsorbed onto the

gold/titanium dioxide coating, the hydroxyl radical oxidizes the contaminant to produce water, carbon dioxide, and other substances. Gold is an oxidation catalyst that lowers the barrier energy of carbon monoxide to oxidize the carbon monoxide to carbon dioxide. Therefore, the gold/titanium dioxide coating can also simultaneously oxidize carbon monoxide to carbon dioxide.

2.8 Preparation of Supported Nano-Gold Catalysts for Selective Hydrogenation of Maleic Anhydride

A series of supported nano-gold catalysts were prepared through a sol-gel method and their catalytic activities for selective hydrogenation of maleic anhydride were investigated. Y. Ma, F. Shi, H. Xiong, Q. Zhang, Y. Deng, from the Centre for Ecological and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Peoples Republic of China, *Huaxue Xuebao* 2004, **62(13)**, 1242. Effects of reaction temperature, reaction solvent, preparation conditions of the catalyst and catalyst reuse were also studied. Their catalyst Au/SiO₂-O(C) exhibited the highest catalytic performance to yield succinic anhydride or di-Et succinate with a selectivity exceeding 99.5%.

2.9 Relationship between Structure and CO Oxidation Activity of Ceria-Supported Gold Catalysts

Gold catalysts supported on cerium oxide were prepared by solvated metal atom dispersion (SMAD), by deposition-precipitation (DP), and by coprecipitation (CP) methods and were characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), and XPS. A. Venezia, G. Pantaleo, A. Longo, G. Di Carlo, M. Casaletto; F.L. Liotta and G. Deganello from the Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Palermo, Italy, *Journal of Physical Chemistry B*, 2005, **109(7)**, 2821. The catalytic activity was tested in the CO oxidation reaction. The structural and surface analyses evidenced the presence of a modified ceria phase in the case of the DP sample and the presence of pure ceria and gold metal crystallites in the case of the SMAD and CP samples. The DP sample, after a mild treatment in air at 393 K, exhibited only ionic gold, and it was very active below 273 K. By comparing the activities of the different catalysts, it is suggested that the presence of small gold particles, as obtained by the SMAD technique, is not the main requisite for the achievement of the highest CO conversion. The strong interaction between ionic gold and ceria, by enhancing the ceria surface oxygen reducibility, may det. the particularly high activity.

2.10 Gold-Base Catalysts Supported on Carbonate For Low-Temperature CO Oxidation

Au/MeCO₃ (Me = Ca, Sr, Ba) catalysts prepared by co-precipitation method were studied for low-temperature CO oxidation in the presence/absence of water in the feed stream. H. Lian, M. Jia, W. Pan, Y. Li, W. Zhang, D. Jiang, from the College of Chemistry, Jilin University, Changchun, Peoples Republic of China, *Catalysis Communications* 2005, **6**(1), 47. The type of support and the calcination temperatures have considerable effect on the activity of the catalysts. Among them, Au/BaCO₃ calcined at 473 K shows the highest activity, full conversion of CO can be obtained at ambient reaction temperature in the presence of moisture. The addition of water vapor in feed stream has positive influence on the activity of Au/MeCO₃ catalysts for CO oxidation, which might be due to water can participate CO oxidation reaction directly.

2.11 Kinetic Study of a Direct Water Synthesis over Silica-Supported Gold Nanoparticles

The reaction mechanism of water formation from H₂ and O₂ was studied over a series of silica-supported gold nanoparticles. D. Barton and S. Podkolzin from the Core Research, The Dow Chemical Company, Midland, USA, *Journal of Physical Chemistry B*, 2005, **109**(6), 2262. The metal particle size distributions were established with TEM and XRD measurements. Hydrogen and oxygen adsorption calorimetry was used to probe the nature and properties of surface species formed by these molecules DFT calculations with Au₅, Au₁₃, and Au₅₅ clusters and with Au(111) and Au(211) periodic slabs were performed to establish the thermodynamic stability and reactivity of surface species. Kinetic measurements were performed by varying the reactant partial pressures at 433 K and by varying the temperature from 383 to 483 K at 2.5 kPa of O₂ and 5 kPa of H₂. The measured apparent power law kinetic parameters were similar for all catalysts in this study: hydrogen order of 0.7-0.8, oxygen order of 0.1-0.2, and activation energy of 37-41 kJ/mol. Catalysts with Si-MFI (Silicalite-1) and Ti-MFI (TS-1 with 1 wt % Ti) exhibited similar activities. The activities of these catalysts with the MFI crystalline supports were 60-70 times higher than that of an analogous catalyst with an amorphous silica support. Water addition in the inlet stream at 3 vol % did not affect the reaction rates. The mechanism of water formation over gold is proposed to proceed through the formation of OOH and H₂O₂ intermediates. A rate expression derived based on this mechanism accurately describes the experimental kinetic data. The higher activity of the MFI-supported catalysts is attributed to a higher concentration of gold particles comparable in size to Au₁₃, which can fit inside MFI pores. DFT results suggest that such intermediate-size gold particles are most reactive toward water formation. Smaller particles are proposed to be less reactive due to the instability of the OOH intermediate whereas larger particles are less reactive due to the instability of adsorbed oxygen.

2.12 Direct Vapor Phase Propylene Epoxidation Over Deposition-Precipitation Gold-Titania Catalysts in the Presence Of H₂/O₂: Effects of Support, Neutralizing Agent, and Pretreatment

The effects of titanium connectivity, deposition solution neutralizing agent, and catalyst pretreatment were examined for a series of Au-on-titanium- containing supports for the direct gas-phase epoxidation of propylene using hydrogen and oxygen. E. Stangland, B. Taylor, R. Andres, W. Delgass, from the Forney Hall of Chemical Engineering, Purdue University, West Lafayette, USA, *Journal of Physical Chemistry B*, 2005, **109**(6), 2321. The degree of titanium isolation was examined using pure titania, monolayer-titania on silica, submonolayer-titania on silica, and titanium silicalite-1 (TS-1) supports. Activity and selectivity were shown to increase as the degree of titanium isolation increased, with TS-1 and submonolayer-titania supports providing the best stability and yield. Isolation of the titanium was found to significantly reduce the cracking of propylene to ethanol and carbon dioxide. Sodium carbonate was found to be the best neutralizing agent for catalysts prepared using deposition-precipitation (DP). DP with ammonium hydroxide gave catalysts with reduced selectivity and activity. Titania-modified silica was found to produce better catalysts when the support was not calcined prior to gold deposition. Similarly, calcination was detrimental to catalysts prepared via deposition of a 2 nm gold colloid onto titania-modified supports even though the gold did not sinter. The beneficial effects of Ti site isolation and support acid/base control are best seen at higher temperatures where only a few catalysts can maintain selectivity.

3 Chemistry

3.1 Hydrophobic, Organically Dispersible Gold Nanoparticles of Variable Shape Produced by the Spontaneous Reduction of Aqueous Chloroaurate Ions by Hexadecylaniline Molecules

In addition to control over the size and monodispersity of nanoparticle, nanomaterial synthesis procedures are increasingly required to control their shape and assembly as well. The authors, P. Selvakannan, S. Mandal, R. Pasricha and M. Sastry from the Materials Chemistry Division, National Chemical Laboratory, Pune, India, *Journal of Colloid and Interface Science* 2004, **279**(1), 124, demonstrate in this paper synthesis of organically dispersible, hydrophobic Au nanoparticles of spherical shape and encased in triangular thin polyaniline shells by doing reaction under static conditions and assembly of these particles onto polymer nanorod/nanowire-like templates by varying the molar ratio of chloroaurate ions to hexadecylaniline and varying the solvent by the spontaneous redn. of aqueous chloroaurate ions by hexadecylaniline mols. in a biphasic reaction setup. Under stationary conditions (no stirring), a biphasic mixture of hexadecylaniline in toluene and

chloraurate ions in H₂O leads to the electrostatic complexation of chloraurate ions with hexadecylaniline at the liq.-liq. interface and their phase transfer into the organic phase, followed by their reduction by the hexadecylaniline molecules. By varying the conditions, the templating action of Au nanoparticles or the polyaniline nanodispersions can be tuned in the organic medium and resulting assembly.

3.2 Surface Chemistry of Gold Nanoparticles Produced by Laser Ablation in Aqueous Media

The femtosecond laser ablation of a Au target in aq. solutions was used to produce colloidal Au nanoparticles with controlled surface chemistry, J.P. Sylvestre, S. Poulin, A. Kabashin, E. Sacher, M. Meunier, J. Luong from the Laser Processing Laboratory, Department of Engineering Physics, Ecole Polytechnique de Montreal, Montreal, Canada *Journal of Physical Chemistry B* 2004, **108(43)**, 16864. A detailed chemical analysis showed that the nanoparticles formed were partially oxidized by the oxygen present in solution. The hydroxylation of these Au-O compounds, followed by a proton loss to give surface Au-O-, resulted in the neg. charging of the nanoparticles. The partial oxidation of the Au nanoparticle surface enhances its chem. reactivity and consequently has a strong impact on its growth. In particular, the oxidized surface reacted efficiently with Cl- and OH- to augment its net surface charge.

This limited the coalescence of the particles, due to electrostatic repulsion, and led to a significant reduction of their size. Taking advantage of the repulsion effect, efficient size control was achieved using different salts (7 ± 5 nm for 10 mM KCl, 5.5 ± 4 nm for 10 mM NaCl, 8 ± 5 nm for NaOH, pH 9.4), a considerable improvement comparatively to particles prepared in deionized H₂O, using identical ablation conditions, where particles of 1-250 nm were produced. The partially oxidized Au surface was also suitable for surface modification through both covalent and electrostatic interactions during particle formation. Using solutions of N-propylamine, the authors showed an efficient control of nanoparticle size (5-8 ± 4-7 nm) by the involvement of these interactions. The results obtained help to develop methodologies for the control of laser-ablation-based nanoparticle growth and the functionalization of nanoparticle surfaces by specific interactions.

3.3 Luminescence Spectra Characters of Nanostructured Gold Thin-Film

Gold colloid was prepared via an electrochemical method. J. Zhao, Y. Wang and J. Zhu from the Institute of Modern Physics, School of Science, Xi'an Jiaotong University, Peoples Republic of China, *Guangpuxue Yu Guangpu Fenxi*, 2004, **24(12)**, 1609. Nanostructured gold thin-films were deposited on glass by using a self-assembled technique. UV-visible spectra and luminescence spectra were measured at room temperature. The absorption spectrum features show two peaks and the longer wavelength one at 610 nm corresponds to linear aggregated gold nanochains. The luminescence

peaks at about 375 nm and 700 nm are due to the local field enhancement via coupling to the transverse and longitudinal surface plasmon resonance from gold nanochains. Both the intensity and no. of the fluorescence emission peaks increase with increasing excited light and the layers no. It is indicated that the nanostructured gold thin-films formed a disordered particles system. Further more, multiple scattering takes place in these self-organized random micro-cavities.

3.4 Adsorption of Silane and Methylsilane on Gold Surfaces

The adsorption of silane and methylsilane on the (1 1 0) and polycryst. surfaces of Au is examined using vibrational electron energy loss spectroscopy (VEELS), angle-resolved UPS (ARUPS), and XPS. M. Spencer, G. Nyberg from the Department of Chemistry, La Trobe University, 3086, Australia, *Surface Science*, 2004, **573(2)**, 151. Adsorption of silane onto the Au(1 1 0) surface at low temperatures is dissociative and yields an SiH₂ and possibly also SiH₃ surface species. Further dissociation occurs at room temperature to yield adsorbed SiH, which is tilted on the surface, with complete dissociation to Si occurring by 110.degree. The similarity in the UP spectra for silane adsorbed on the polycrystalline sample suggests that the same surface species are present over that temperature range. Above 200.degree., spectral changes suggest rearrangement of the Si atoms, which, by 350.degree., have diffused into the bulk. Adsorption of methylsilane onto the (1 1 0) surface at low temperatures initially produces adsorbed CH₃SiH or CH₃SiH₂, with undissociated methylsilane physisorbing at higher exposures. By room temperature, desorption and decomposition leaves (or direct adsorption yields) only adsorbed CH₃Si. After further heating, the H-C bonds of the CH₃ group break to leave an adsorbed SiC species. On the polycrystalline surface, methylsilane adsorption is the same at low temperatures as on (1 1 0). In contrast to the latter, though, the UP spectra indicate that direct exposures at room temperature yield adsorbed Si or SiC initially, with CH₃Si again adsorbing at higher exposures. Upon further heating to 330.degree., little if any methyl-groups remain on the surface and the Si has started to diffuse into the bulk.

4 Electrochemistry

4.1 Electroless Plating Solution for Gold on Copper Electric or Electronic Parts

R. Washimi, H. Watanabe and K. Kojima from the Kojima Chemicals Co., Ltd., Japan, Patent No. JP 2004323963, A2, 18.11.2004 describe an invention where the plating solution contains organic acid (succinic acid, phthalic acid, fumaric acid, maleic acid, and/or malonic acid) or their salt, erythorbic acid or its salt, K cyanide, and Au ion source. Preferably, the concentration of the organic acid or its salt is 10-50 g/L; the concentration of erythorbic acid or its salt is 0.1-5 g/L; the concentration of the Au ion source is 0.50-3 g/L; and the Au ion source is gold potassium cyanide, gold sodium cyanide, chlorauric acid, Au sulfite, or Au thiosulfate.

4.2 An Electrochemical Quartz Crystal Microbalance Study of The Etching of Gold Surfaces In the Presence of Tetramethylthiourea

The oxidation of tetramethylthiourea (TMTU) at Au electrodes in MeCN, leading to dissolution of the electrode, was studied by electrochemical methods and by an electrochemical quartz crystal microbalance (EQCM). A. Larsen, K. Johannsen and K. Gothelf from the Center for Catalysis and Interdisciplinary Nanoscience Center at Aarhus Denmark, *Journal of Colloid and Interface Science* 2004, **279(1)**, 158. TMTU in MeCN readily adsorbs at Au electrodes and an estimated coverage of 5.5.times.10⁻¹⁰ molcm⁻² (30 .ANG.2 per mol.) was measured electrochemically. Nevertheless, the oxidation of TMTU in solution is a diffusion-controlled process and is strongly influenced by the electrode material, as observed by comparison of Au electrodes with glassy C and Pt working electrodes.

In the absence of TMTU, EQCM cyclic voltammetry experiments showed dissolution of Au through a 1e⁻ oxidation process at potentials more positive than 1.20 V vs. SCE. Potential step and cyclic voltammetry EQCM experiments performed using Au surfaces in the presence of TMTU revealed TMTU-assisted etching of Au at potentials .gtoreq.0.35 V vs. SCE. In the potential region from 0.35 to 1.20 V the current response of TMTU oxidation mimics the response expected for a redox-active species in solution, including the presence of a mass-transfer-limited region, which supports the conclusion that the etching process in this potential region is initiated by the oxidation of TMTU at the Au surface. The current efficiency of the TMTU-assisted etching was found to vary between 12 electrons per Au atom dissolved (e/Au) (E = 0.50 V vs. SCE) and 2 e/Au (0.90 V<E<1.20 V). At potentials <0.90 V the dominant electrochemical process is the formation of TMTU⁺, whereas at higher potentials the etching of the Au surface by formation of a Au(I)-TMTU⁺ species becomes equally important. At potentials 1.20 V the etching is no longer dependent on the diffusion of TMTU and the e/Au value approaches 1.

4.3 Formation of Gold Nanoparticles Supported on Carbon Nanotubes by Using an Electroless Plating Method

Gold nanoparticles supported on carbon nanotubes (CNTs) were obtained by using an electroless plating technique. X. Ma, N. Lun and S. Wen from the School of Chemistry and Chemical Engineering, Shandong University, Peoples Republic of China, *Diamond and Related Materials* 2005, **14(1)**, 68. High-resolution transmission electron microscopy evidenced the high-d. and homogeneous dispersion of spherical gold nanoparticles on the outer surfaces of the carbon nanotubes, with a sharp particle size distribution centered at around 3-4 nm of diameter. The resultant hybrid nanostructures have potential application for being used as novel gold nanocatalysts.

4.4 Gold and Silver Micro-Wire Electrodes for Trace Analysis of Metals

Micro-wire electrodes were made from Au and Ag wires (diameter: 25 .mu.m; length: 3-21 mm) and sealed in a polyethylene holder; micro-disk electrodes were made from the same wires and polished. The Au electrodes were electrochemically coated with Hg before use; the Ag wires were used without coating. G. Billon and C. van den Berg from the Department of Earth and Ocean Sciences, University of Liverpool, UK *Electroanalysis*, 2004, **16(19)**, 1583.

Comparative measurements demonstrated that the micro-wire electrodes had much higher sensitivity, and a much (10-100 .times.) lower limit of detection, than micro-disk electrodes, and the sensitivity increased linearly with the area and length of the electrodes. Using a Au micro-wire electrode of 21 mm and a deposition time of 300 s the limit of detection was 0.07 nM Pb in seawater of natural pH, compared to a limit of detection of 10 nM Pb (more than 100 .times. greater) using a Au micro-disk electrode of the same diameter. Using the Ag micro-wire electrode the limit of detection of lead was improved by a factor of 10 to 0.2 nM in acidified seawater. It is expected that the improved sensitivity of micro-wire electrodes will lead to successful *in situ* detection of metals in natural waters.

4.5 Electroreduction of Peroxyacetic Acid at Gold Electrode in Aqueous Media

The kinetics of electroreduction of peroxyacetic acid (PAA) was studied at a Au electrode in acetate buffer solutions of pH in the range 3-6. M. Awad, A. Denggerile and T. Ohsaka from the Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Japan, *Journal of the Electrochemical Society*, 2004, **151(12)**, E358. The electroreduction of PAA was irreversible. The relevant kinetic parameters including the Tafel slope, the std. rate const. (k₀), the electrochemical reaction order (m), (.alpha.n) of the transfer coefficient and the number of electrons involved in the rate-determining step, and the no. (n) of electrons involved in the overall electrode reaction were detected using cyclic voltammetry, hydrodynamic voltammetry, and hydrodynamic chronocoulometry. The Tafel slope = 0.215 V/decade, m = 1, k₀ = 9.4 .times. 10⁻¹¹ cms⁻¹, .alpha.n a = 0.32, and n = 2. The formal potential of the PAA/HOAc redox couple was also theoretical calculated to be 1.762 V vs. Ag/AgCl based on the equilibrium constant for the reaction of PAA and H₂O₂ in the presence of acid catalyst and the std. redox potential of H₂O₂. The diffusion coefficient of PAA was also established. Based on the obtained results, the overall electroreduction of PAA is considered to be composed of 2 1-electron reduction steps with the formation of acetate or hydroxyl radical as probable reaction intermediates.

5 Electronics and Sensors

5.1 Fabrication of Conductive Gold Films on Flexible Polymer substrates by Self-assembly

A method of fabricating conductive gold films on mech. flexible polymer substrates was developed by L. Supriya and R.O. Claus from the Fiber and Electro-Optics Research Center, Virginia Polytechnic Institute and State University, Blacksburg USA, *Polymeric Materials: Science and Engineering*, 2004, **91**, 18. This involves the surface modification of the polymer by functionalized silanes, like amino- and mercapto-, which are used to attach the colloidal gold particles to the polymer. Argon plasma treatment of the polymer creates long-lived free radicals on the surface, which when exposed to air form hydroperoxyl groups. The silanes are attached to the polymer via these groups forming a monolayer, with the functional groups on the outside. This silane coated substrate is dipped in colloidal gold solution, when the particles are bound to the surface. Conductive layers are formed by reducing more gold onto the attached gold, in solution. Films were successfully assembled on polyethylene and Kapton- with a surface resistance of 1 .OMEGA./sq. The films do not delaminate upon rinsing the substrate with water or ethanol, or by twisting or bending it.

5.2 Angular Dispersion of Protons Transmitted Through Thin Gold Films

The angular distributions of protons travelling through thin polycrystalline gold targets (.approximately 15 nm) with incident energies in the range of 4-10keV have been measured. C. Archubi, C. Denton, J. Eckardt, G. Lantschner, F. Lovey, J. Valdes, C. Parra, F. Zappa and N. Arista from the Division Colisiones Atómicas, Centro Atómico Bariloche, Instituto Balseiro, Bariloche, Argentina *Physica Status Solidi B: Basic Research* 2004, **241(10)**, 2389. The results confirm previous experiments at higher energies showing deviations from theoretical predictions based on the standard multiple scattering theory. In order to prove that the effect of crystal structure is one of the main causes of these deviations the authors have performed numerical simulations. To simulate the polycrystalline structure in a realistic way, the authors have made an analysis of the target by means of transmission electron microscopy (TEM) techniques. Including these characteristics in the simulation, together with the effect of vibrations and crystal disorder they analyzed the corresponding angular distribution. To evaluate the role of channeling, they also measured angular distributions of protons in a .ltbbrac.100.rtbbrac. gold foil and made the corresponding numerical simulations. The results show the critical influence of the target structure in the angular spectra of transmitted ions.

5.3 Ab Initio Study of the Electric Transport In Gold Nanocontacts containing Single Impurities

By employing a real-space formulation of the Kubo-Greenwood equation based on a Green's function embedding technique combined with the fully relativistic spin-polarized Korringa-Kohn-Rostoker method a detailed investigation of the electric transport through atomic-scaled contacts between two Au(001) semi-infinite systems is presented. K. Palotas, B. Lazarovits, L. Szunyogh and P. Weinberger from the Center for Computational Materials Science, Vienna University of Technology, Vienna, Austria, *Physical Review B: Condensed Matter and Materials Physics*, 2004, **70(13)**, 134421/1. Following a careful numerical test of the method the conductance of Au nanocontacts with different geometries is calculated and, in turn, correlated with the thickness of the constriction. Particular emphasis is paid to the influence of transition metal impurities (Pd, Fe, and Co) placed on various positions near the center of a particular contact. We found that the conductance is very sensitive to the position of the magnetic impurities and that the mechanism for the occurring relative changes can mainly be attributed to the impurities' minority d-band inducing resonant line shapes in the s-like d. of states at the center of the contact.

5.4 Fabrication of Folding Microstructures Actuated by Polypyrrole/Gold Bilayer

A method was developed for fabrication of folding microstructures using a polypyrrole/gold bilayer as actuator. Y. Liu, L. Oh, S. Fanning, B. Shapiro, E. Smela from the Department of Mechanical Engineering, University of Maryland, College, USA, Transducers '03, International Conference on Solid-State Sensors, Actuators and Microsystems, Digest of Technical Papers, 12th, Boston, MA, United States, June 8-12, 2003, **1**, 786. A series of bilayers is defined on one surface of the substrate (Cr adhesive layer on Kapton sheet), with an interlocking Al layer, and hinges are formed by etching the substrate from the back side to undercut the bilayers. A shape-morphing object is demonstrated that comprises multiple hinges. This object was able to bend both forward and backward. The technology can be used to fabricate medical devices that operate in bio-fluids.

6 Medical and Dental

6.1 Amalgam fillings with inert coating, preferably gold

The invention by W. Hasenpusch, Patent No. DE 202004013405 U1, 1.12.2004, concerns a model of an inert amalgam filling, releasing distinctly less mercury due to application of a cold-welded metal layer on the surface; gold is preferably applied. Gold can be layered as gold leaves, gold powder or prepared from gold chloride and sodium thiosulfate-containing paste in the presence of ascorbic acid; the paste is placed on the top of the ready amalgam filling.

6.2 Gold Suture and Method of Use in Wound Closure

B. Wolf, I. Bogin, R. Bogin, USA, Patent No US 2004267314, A1 30.12.2004 have invented a method of wound closure comprising providing a gold suture and closing the laceration with the gold suture. The laceration is closed by inserting the suture into the dermis and through the s.c. fat layer on one side of the laceration, inserting the suture at the base of the laceration, inserting the suture through the s.c. fat layer and into the dermis on the other side of the laceration to form a loop under the skin, repeating the steps in another insertion 3-5 mm from the loop in a continuous or interrupted manner to close the laceration and tightening the suture line by applying tension to the loops to bring one side of the laceration into contact with the other side of the laceration.

6.3 Patterned Networks of Mouse Hippocampal Neurons on Peptide-Coated Gold Surfaces

Patterned networks of hippocampal neurons were generated on peptide-coated gold substrates prepared by microscope projection photolithog. and microcontact printing. D. Heller, V. Garga, K. Kelleher; T. Lee, S. Mahbubani, L. Sigworth, T. Lee, M. Rea from the Center for Material Chemistry, Department of Chemistry, University of Houston, USA, *Biomaterials*, 2004, **26(8)**, 883. A 19 amino acid peptide fragment of laminin A (PA22-2) that includes the IKVAV cell adhesion domain was used to direct patterns of cell adhesion in primary culture. Microscale grid patterns of peptide were deposited on gold-coated glass cover slips by soft lithog. using "stamps" fashioned from polydimethylsiloxane. Strong coordination bonding between gold atoms on the surface and the sulfur atoms of the N-terminal cysteine residues supported stable adhesion of the peptide, which was confirmed by immunofluorescence using anti-IKVAV antiserum. Dispersed hippocampal cells isolated from neonatal mouse pups were grown on peptide-patterned gold substrates for 7 days. Neurons preferentially adhered to peptide-coated regions of the gold surface and restricted their processes to the peptide patterns. Whole cell recordings of neurons grown in patterned arrays revealed an average membrane potential of -50 mV, well as the presence of voltage-gated ion conductances. Peptide-modified gold surfaces serve as convenient and effective substrates for growing ordered neural networks that are compatible with existing multi-electrode array recording technology

7 Metallurgy, Materials and Coatings

7.1 The Effects of Ca and Pd Dopants on Gold Bonding Wire and Gold Rod

There is currently little information regarding the physicochemical effects of common bonding wire dopants such as Ca and Pd despite the use of gold bonding wire as an electrical interconnection in over 80% of semiconductor devices. This paper by T. Saraswati, T. Sritharan, C. Pang, Y. Chew, C. Breach, F. Wulff, S. Mhaisalkar and C. Wong from the School of Materials Engineering, Nanyang Technological

University, Singapore, *Thin Solid Films* 2004, **462-463**, 351, presents experimental results on the residual microstrains in 4 N gold bonding wires with different concentrations of Ca-Pd, measured using peak broadening in X-ray diffraction. The effect of Ca was found to be more prominent. In order to understand more about the physicochemical action of Ca and its effects on the microstructure, TEM and depth sensing nanoindentation (DSI) were used to study 2 mm Ca-doped hard-drawn rods.

7.2 The Strength of Gold Nanowires

Atomistic simulations are used to investigate the yield strength of experimentally observed at. and nanometer scale gold wires. K. Gall, J. Diao, M. Dunn from the Department of Mechanical Engineering, University of Colorado at Boulder, USA *Nano Letters* 2004, **4(12)**, 2431. The atomistic predictions of strength are quant. consistent with discrete experimental measurements and they reveal the mechanisms for increasing nanowire strength with decreasing dimensional scale. Distinct transitions in yield strength and yield mechanism are discovered. At nanometer scales (diam. > 1 nm), the mechanism for strengthening involves the scarcity and low mobility of dislocations coupled with constraint from tensile surface stresses. As the wires approach the at. scale (diam. < 1 nm), an increase in strength occurs concurrent with a surface-stress-induced change in the stable structure of the nanowires and the absence of dislocation-mediated yield. The results constitute a new fundamental understanding of strength in metallic nanowires spanning technology relevant dimensional scales.

7.3 Synthesis of Gold Nanorods and Nanowires by a Microwave-Polyol Method

HAuCl₄ was reduced by ethylene glycol, in the presence of polyvinylpyrrolidone (PVP) under microwave (MW) heating in a continuous wave (CW) mode for 2 min. M. Tsuji, M. Hashimoto, Y. Nishizawa and T. Tsuji from the Institute for Materials Chemistry and Engineering, Kyushu University, Japan, *Materials Letters*, 2004, **58(17-18)**, 2326. Dominant products were polygonal nanoplates and close-to-spherical nanoparticles of gold. In addn., small amounts of single crystal gold nanorods and nanowires (0.5-3% of total no. of products) with diameters of 20-100 nm and lengths of 0.6-5 .mu.m were produced. The diameter and length of gold nanorods and nanowires could be controlled by changing the HAuCl₄.cntdot.4H₂O/PVP ratio. The formation mechanism of anisotropic gold nanostructures was discussed.

8 Nanotechnology

8.1 Functionalized gold nanoparticles chemisorbed by organic .pi.-ligands and their networked structures

A review in Japanese by T. Sugawara from the Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Japan, *Yuki Gosei Kagaku Kyokaishi* 2004, **62(5)**, 447. Thiol-derivatized Au nanoparticles has drawn much attention as a building block of nano-scaled electronic devices. As a functional thiol ligand, .pi.-conjugated radical thiols, e.g. p-mercaptophenyl nitronyl nitroxide, etc., have been synthesized. Nanoparticles with the average particle size of 4 nm were chemisorbed by 100 ligands of p-mercaptophenyl nitronyl nitroxide and they were isolated and characterized. The ESR spectral peak width of the radical thiol on the nanoparticle was extremely broadened ($\Delta H_{pp} = 30$ mT at RT), suggesting the significant magnetic interaction between an unpaired electron of the radical unit and conduction electrons of Au nanoparticles. Network structures of Au nanoparticles connected by .sigma.- or .pi. mol. nanowires made of alkanedithiol or oligothiophene with protected thiol groups were also prepared. It is to be noted that the network structures of nanoparticles connected with mol. wires were prepared through a self-organization process. They are semiconductors with small activation energies (.apprx.20 meV at temps. >40 K, and .apprx.6 meV at <40 K), suggesting a hopping mechanism for the electronic transportation in a higher temps. region ($T = 40$ K) and a tunneling mechanism in the lower temp. ($T < 40$ K).

8.2 Crystal Growth of Gold Nanoparticles on Indium Tin Oxides in the Absence and Presence of 3-Mercaptopropyltrimethoxysilane

By applying a seed-mediated growth method, which was developed for chemical synthesis of Au nanorods in aqueous solution, the authors observed the changes in the crystal growth of Au nanoparticles on the surfaces of In Sn oxides (ITO) in the presence and absence of 3-mercaptopropyltrimethoxysilane (MPTMS). M. Kambayashi, J. Zhang and M. Oyama from the Division of Research Initiatives International Innovation Center, University Kyoto, Japan, *Crystal Growth & Design* 2005, **5(1)**, 81. While flat and amorphous-like growth of Au nanoparticles were observed on the MPTMS layer-modified ITO due to the interaction with the thiol group, in the absence of the MPTMS layer, Au nanoparticles grow relatively freely to form the crystal-like structures in the solution phase at the ITO surface. The Au nanoparticle-modified ITO surfaces prepared under the latter conditions are promising as new functional interfaces, because Au nanoparticles could be attached on the surfaces without using binder mols., such as MPTMS.

8.3 Preparation and Characterization of Highly Dispersed Gold Nanoparticles within Channels of Mesoporous Silica

The preparation of highly dispersed gold nanoparticles in mesoporous silica, SBA-15 is monitored by in situ XAS measurement. K. Chao, M. Cheng, Y. Ho and P. Liu from the Department of Chemistry, National Tsinghua University, Hsinchu, Taiwan, *Catalysis Today* 2004, **97(1)**, 49. The silanation of intrachannel surface with TPTAC can generate ion-exchange sites for anionic $\text{Au}(\text{OH})\text{nCl}_{4-\text{n}}$ (with $\text{n} = 0-4$) complex ions and help to produce uniformly dispersed gold nanoparticles in the host channels after further reduction. The average size of metal nanoparticles is dependent on the pH value of gold precursor solution.

8.4 Morphologically Well-Defined Gold Nanoparticles Embedded In Thermo-Responsive Hydrogel Matrices

Nanocomposite materials consisting of colloidal gold (Au) nanoparticles embedded in thermo-responsive poly(N-isopropylacrylamide) (PNIP Am) hydrogels were synthesized by C. Wang, N. Flynn and R. Langer from the Department of Chemical Engineering, Massachusetts Institute of Technology, USA. *Materials Research Society Symposium Proceedings* 2004, **820** (Nanoengineered Assemblies and Advanced Micro/Nanosystems), 333. Thiol groups that bind to both Au^{3+} ions and colloidal Au are incorporated into the side-chains of the PNIPAm hydrogels through copolymerization. This report describes formation of morphology well-defined Au nanoparticles with varying long-term stability inside the hydrogel matrixes containing adjustable concentrations of thiols. Compared with the non-Au containing PNIPAm hydrogels, the Au-PNIPAm nanocomposite hydrogels have shown higher degrees of equil. swelling and different temperature-triggered phase transitions. It is hypothesized that these remarkable changes in hydrogel bulk properties are related to the different morphologies and sizes, and possibly the amount of surface charges, of the Au nanoparticles.

8.5 Synthesis of Polysaccharide-Stabilized Gold and Silver Nanoparticles: A Green Method

A simple, green method was developed by H. Huang and X. Yang from the Changchun Institute of Applied Chemistry, State Key Laboratory of Electroanalytical Chemistry, Chinese Academy of Sciences, Changchun, Peoples Republic of China *Carbohydrate Research* 2004, **339(15)**, 2627, for the synthesis of gold and silver nanoparticles by using polysaccharides as reducing/stabilizing agents. The obtained positively charged chitosan-stabilized gold nanoparticles and negatively charged heparin-stabilized silver nanoparticles were characterized with UV-vis spectroscopy and transmission electron microscopy. The results illustrated the formation of gold and silver nanoparticles inside the nanoscopic polysaccharide templates. Moreover, the morphology and size distribution of prepared gold and silver nanoparticles varied with the concentration of both the polysaccharides and the precursor metal salts.

8.6 Structural transitions in nanometer-sized gold

A review. About forty years ago it was discovered that the nanometer-sized gold forms two types of fivefold symmetry morphologies, icosahedron (Ih) and decahedron (Dh). However, until now, no clear-cut experimental result has been provided about the fundamental question: "At what size do these non-crystalline structures change to the ordinal crystal". The author, K. Koga from the Nano-Technol. Res. Div., Natl. Inst. Adv. Ind. Sci. Technol., Tsukuba, Japan *Nippon Butsuri Gakkaishi* 2004, **59(11)**, 776, clarifies this issue by performing statistical structural analyses for gold nanoparticles annealed in the helium heat bath. During this work, he discovered a novel solid-solid transition, Ih-to-Dh transformation, taking place at high temperatures.

9 Refining

9.1 Experimental Study on Recovery of Gold, Silver and Sulfur from Gold Tailing

In the study of the technology of recovering gold, silver and sulfur from gold tailing, a new patent centrifugal concentrator was developed which could drain both heavy and light minerals continuously at the same time. H. Su, R. Jiang and Y. Gu from the Daluohang Gold Mine of Penglai County, Penglai, Shandong Province, Peoples Republic of China, *Huangjin* 2003, **24(8)**, 31.

It was referred to as twin-drainage centrifugal concentrator. As a primary concentration equipment, it was used cooperatively with table concentrator so that the fine-grained minerals could be recovered effectively. The application of this type centrifugal concentrator made the process flow simplified, unsized tailing millable with great treatment capacity, and obtained high recovery rate and marked economic benefit.

9.2 Experimental Study on the Gold Extracted from Carbonaceous Gold Ore Leached in Heaps by Preoxidized Roasting

The preoxidized roast process and direct leaching in heaps of the roasted ore from a low-sulfur carbonaceous silicified gold mine in Dandong, Liaoning Province were studied experimentally. C. Wang, S. Zhou, S. Zhang, H. Yang from the School of Resource & Civil Engineering, Northeastern University, Shenyang, Peoples Republic China, *Dongbei Daxue Xuebao, Ziran Kexueban*, 2004, **25(2)**, 171. The roasted/oxidized conditions of gold ore and main influencing factors on leaching rate of gold were investigated under different temperatures, atmospheres and times, such as the wt.% of NaCN, spraying intensity, grain size of roasted ore and spraying time. As a result, the oxidizing rate and ashing rate of the sulfides and carbonaceous material can be up to 98% and 97%, respectively, if roasting the ore for 1 h (for dearsenification) at 450.degree. and ventilated with small amounts of air to provide 5-10% of oxygen content in air and, further, roasting it for 2 h at 650.degree. and ventilated with full air. The leaching rate of gold is 84.8% if the wt.% of

NaCN is 0.1-0.15%, spraying intensity 15 L/(m².cntdot.h), grain size of roasted ore 0-3 mm and spraying time 8-10 days. The basic technology process of direct leaching in heaps of roasted ore is recommended with the intention of laying a foundation for industrial applications.

10 General

10.1 Preparation of concentrated gold nanoparticle paste and its application to paint colorant

A novel preparation method of concentrated gold nanoparticle pastes was developed. H. Kamo, H. Ishibashi, T. Kobayashi from the Nippon Paint Co., Ltd., Japan, *Shikizai Kyokaishi* 2003, **76(12)**, 469. A comb-shaped block copolymer was used to prevent the mutual coagulation of gold particles. Certain kinds of amines were found to reduce Au³⁺ ion at an industrially preferable and controllable rate. The max. metal concentration in the paste was 20% and the paste also contained 10% of the protective polymer. Gold nanoparticles having diameter of a few lens nanometer were known to exhibit red color due to plasmon light absorption. The gold nanoparticle paste obtained in this study was applied as a paint colorant and proved to show an aesthetic color and high weather durability.

10.2 Decorating of Glass By Bright Gold

A review of decorating of glass by bright gold. L. Rybarikova, J. Kochankova, H. Hradecka from Prague, Czech Republic *Sklar a Keramik*, 2004, **54(3)**, 45. The knowledge following from long-term experience in preparation of this type of decoration is summarized especially with respect to the quality of gold layer. There are also mentioned theoretical ideas about the relation between glass surface and layer of gold resulting from general ideas about adhesion and creation of intermediate layers. The knowledge about the influence of additive metals in bright gold preparation on creation and quality of the gold layer is summarized. Also some results of the study of morphol. and compn. of a gold layer are included.

10.3 Laser Curing of Gold Nanoparticle Inks

The concept of effective laser curing of nanoparticle suspensions (NPS) with a laser beam is presented in this paper. J. Chung, S. Ko, N. Bieri, C. Grigoropoulos, D. Poulikakos, Dimos from the Department of Mechanical Engineering, University of California, Berkeley, USA, *HTD (American Society of Mechanical Engineers)* 2003, **374-3**, 131. A toluene solvent is employed as the carrier of gold nanoparticles possessing a lower melting temperature than that of bulk gold. Using a modified drop-on-demand jetting system, the gold nanoparticle suspended solution is printed on a glass substrate, and cured with laser irradiation. The laser energy coupling to the nanoparticles in conjunction with thermocapillary effects and the evaporation of the solvent are critical to the quality of the electric conductive gold micro-lines. By employing a intensity-modulated double

laser beam processing scheme, to optimize the curing process, it is demonstrated for the first time, that the gold nanoparticles could be sintered on a glass substrate to form a gold line of resistivity close to that of bulk gold. This is a noticeable result, compared to recently published microconductor manufacturing, with nanoparticle suspensions with oven or low power single laser beam curing reporting resistivities four to five times higher than that of bulk gold. As a consequence, in addition to their scientific value, the current results demonstrate the potential of laser printing for use in the microelectronics manufg. for the first time. It was also shown that the morphology of the gold line could be modified by appropriate design of the shape of the processing laser beam.